

U.S. DEPARTMENT OF ENERGY'S (DOE)
VEHICLE TECHNOLOGIES OFFICE (VTO)
2020 ANNUAL MERIT REVIEW (AMR)



**DIRECT CATHODE RECYCLING:
MATERIAL SEPARATION AND PREPARATION**

**RECELL CENTER FOR ADVANCED BATTERY
RECYCLING**



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bat464
Virtual Poster
June 1-4, 2020

PROJECT OVERVIEW

Timeline

- Project start: October 2018
- Project end: September 2021
- Percent complete: ~50%

Budget

FY19	\$4,615k
FY20	\$5,150k

Barriers

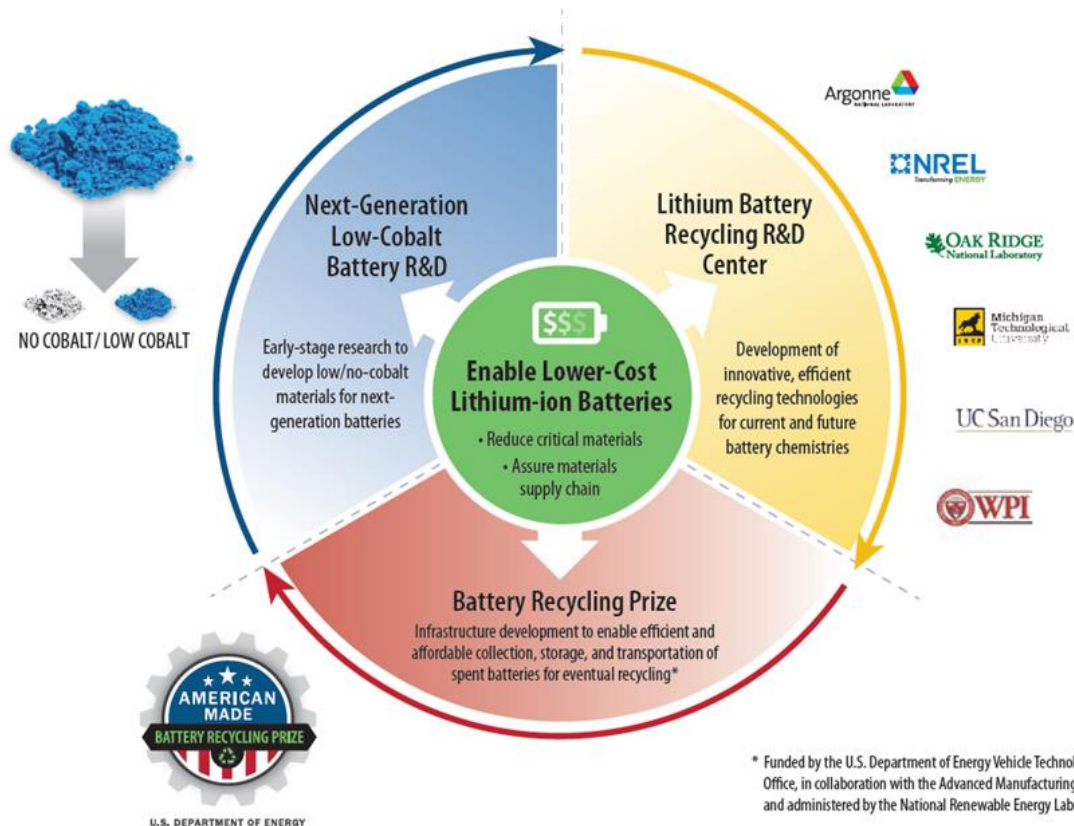
- Recycling and Sustainability
 - Cost to recycle is currently 5-15% of battery cost
 - Material shortage (Li, Co, and Ni)
 - Varying chemistries result in variable backend value

Partners

- Argonne National Laboratory
- National Renewable Energy Laboratory
- Oak Ridge National Laboratory
- University of California, San Diego
- Worcester Polytechnic Institute
- Michigan Technological University

RELEVANCE

- Lower cost of batteries
- Enable lower environmental impacts
- Increase our country's energy security



* Funded by the U.S. Department of Energy Vehicle Technologies Office, in collaboration with the Advanced Manufacturing Office, and administered by the National Renewable Energy Laboratory

APPROACH

Year 1 – Bench scale testing:
Powder-to-Cell



Year 2 – Start to scale up
unit operations

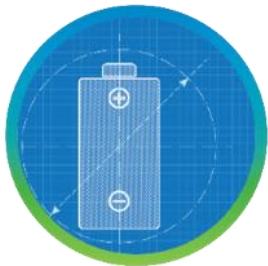


Year 3 – Finish scale up and
show cell-to-cell recycling



**DIRECT
CATHODE
RECYCLING**

**OTHER
MATERIAL
RECOVERY**



**DESIGN
FOR
RECYCLING**

**MODELING
AND
ANALYSIS**



ReCell does not include battery dismantling, transportation, or 2nd use

PROGRAM MILESTONES

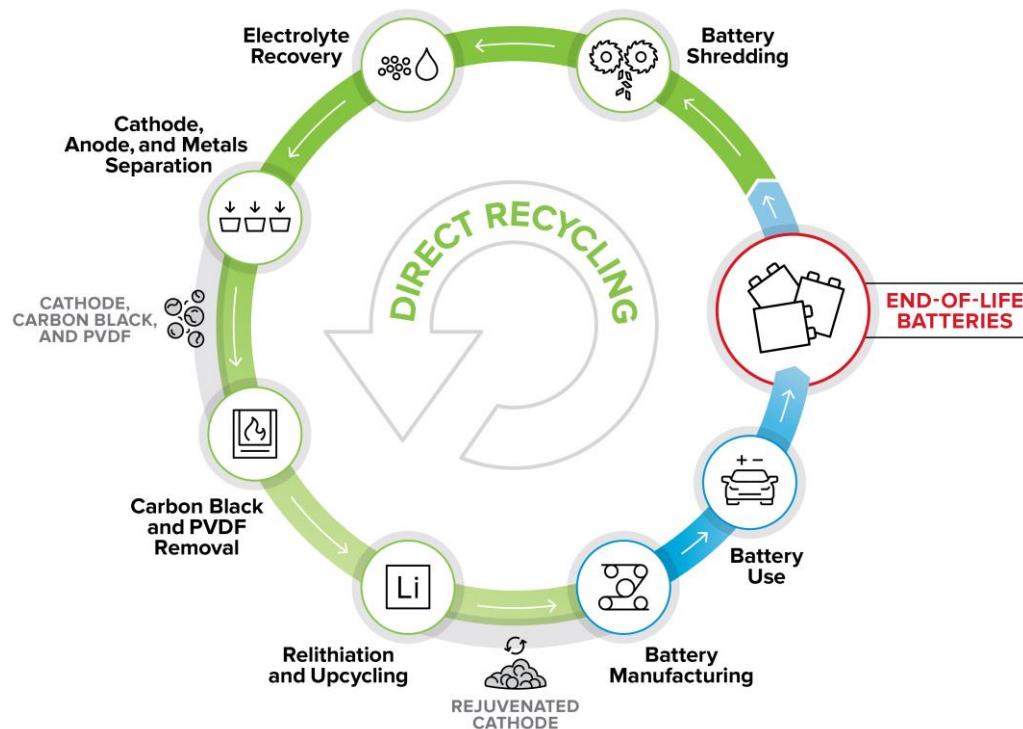
- FY19 Q1 **Complete** Establish the battery recycling center's mission and include its targets and goals
- FY19 Q2 **Complete** Provide an initial progress report on roll-to-roll relithiation
- FY19 Q3 **Complete** Provide an initial progress report on design for recycle initiative
- FY19 Q4 **Complete** Establish the ReCell Center's Battery Recycling Laboratory and Scale-up Facility
-
- FY20 Q1 **Complete** Electron Backscatter Diffraction data comparison of various chemically delithiated NMC-111 versus pristine NMC-111
- FY20 Q2 **Complete** All five relithiation processes added to EverBatt at lab scale and production scale
- FY20 Q3 **Ongoing** Down-select solvent(s) to separate black mass from current collector and optimize the process conditions to achieve >90% recovery of black mass
- FY20 Q4 **Ongoing** Demonstrate recovery of anode and cathode powders using the new pilot scale froth column

Each Individual project has its own milestones that are not listed here.

PREPARING RECYCLED CATHODE MATERIALS FOR RELITHIATION AND UPCYCLING

THE NEED FOR PREPROCESSING

- After shredding and initial separation the cathode material still has issues that need to be addressed
 - Removal of the binder and carbon black
 - The cathode could be a mixture of different compositions that need to be separated
 - Contamination of metals or other materials from the previous steps
 - An understanding of the effects can allow for impurity limits to be developed



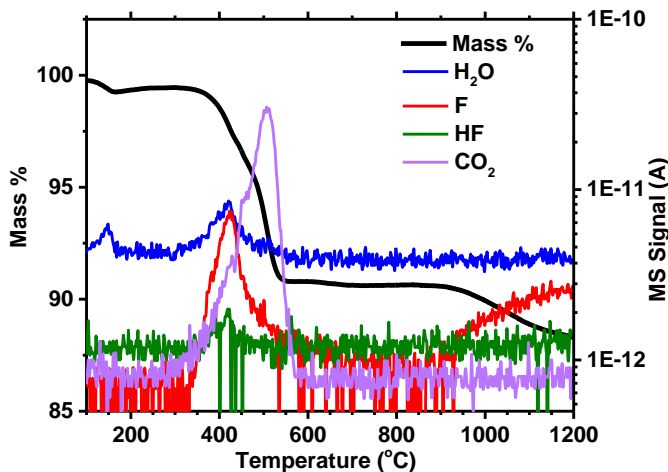
APPROACHES TO BINDER REMOVAL

■ Thermal Decomposition

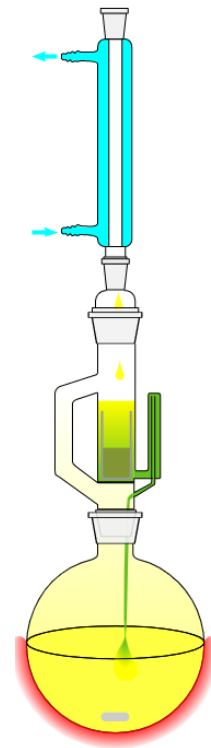
- Heat the material to decompose the PVDF and carbon black to HF, H₂O and CO₂
- Manage the HF to prevent it from reacting detrimentally with the cathode material

■ Solvent Extraction

- Utilize reduced toxicity solvents
- Recover the used solvent using a process such as Soxhlet extraction
- Can recover the PVDF for additional revenue



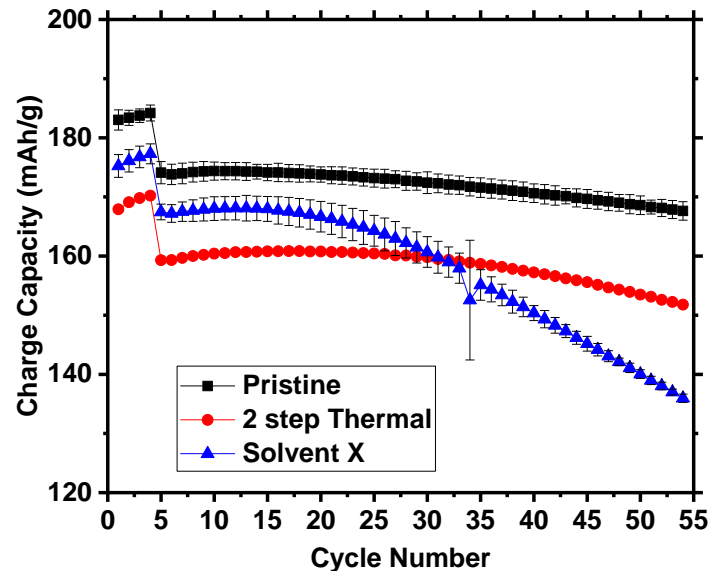
Thermal Decomposition



Solvent Extraction

EXTENDING THERMAL BINDER REMOVAL TO NMC 622

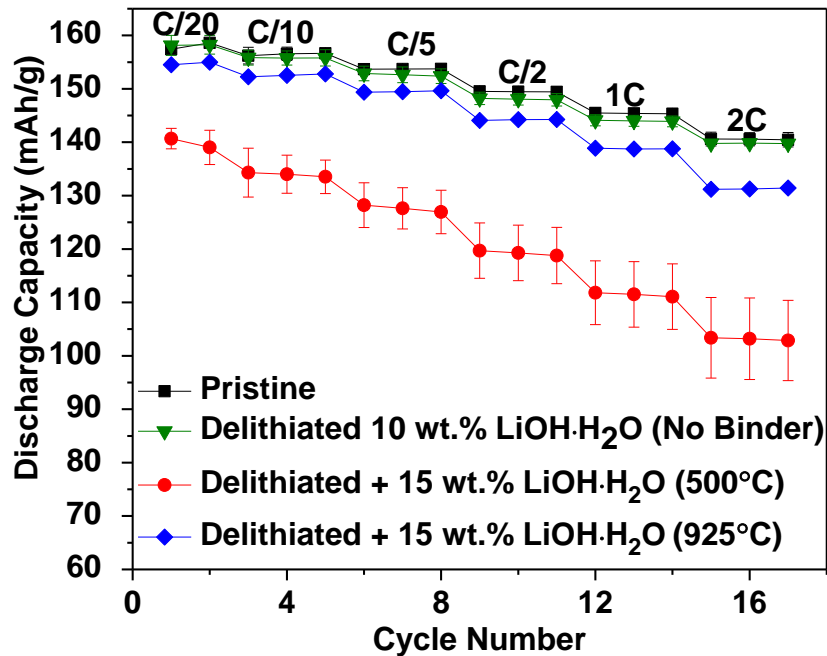
- Previously shown successful thermal binder removal on pristine NMC 111 materials
 - Combining the thermal binder removal process with delamination processes can start to create a more complete recycling process
 - Delamination can be accomplished by either thermal or a solvent X based process
- Higher Ni content NMC materials create a larger challenge due to the increased phase instability
- Requires higher temperatures and additional $\text{LiOH}\cdot\text{H}_2\text{O}$ to reverse any phase changes
 - Further optimization is needed to improve cyclability and initial capacity



NMC 622 mixed with 3 wt.%
PVDF and 3 wt.% carbon
black processed at 750°C with
8 wt.% $\text{LiOH}\cdot\text{H}_2\text{O}$

A ONE-STEP PROCESS FOR BINDER REMOVAL AND RELITHIATION

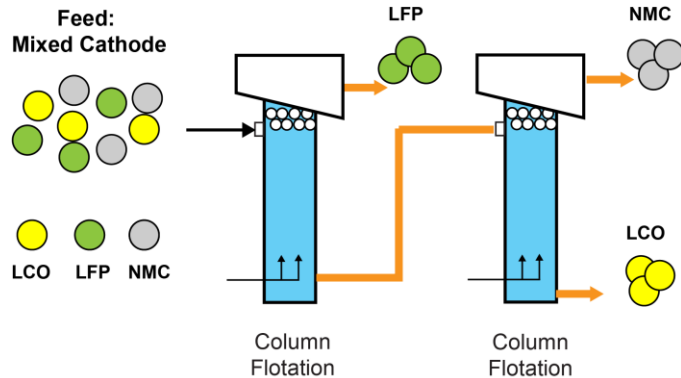
- Delithiated materials are more unstable than fully lithiated materials
- Without binder the delithiated NMC 111 can be relithiated at 500°C with $\text{LiOH}\cdot\text{H}_2\text{O}$
- Adding enough $\text{LiOH}\cdot\text{H}_2\text{O}$ for relithiation and binder removal with 500°C process results in poor performance
- Requires higher temperatures to reverse phase changes that occur during the initial binder removal



10% Chemically Delithiated NMC 111
mixed with 3 wt.% PVDF and 5 wt.%
carbon black processed at 500°C

CATHODE SEPARATION VIA FROTH FLOTATION

- Froth flotation is a scalable process that separates materials by differences in the hydrophobicity
- A variety of additives, called collectors, can be added to modify the materials hydrophobicity



Multistep Froth Flotation Separation Process

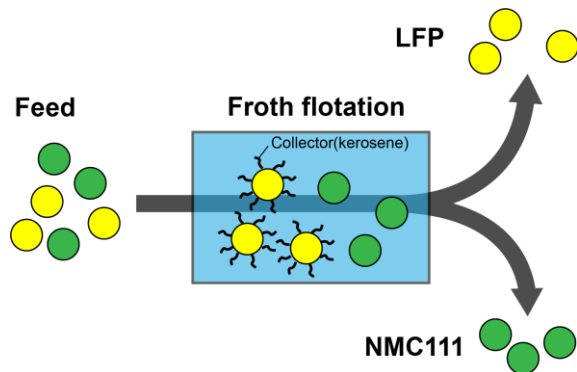
	LFP	LMO	LCO	NCA	NMC111	NMC811
LFP						
LMO						
LCO						
NCA						
NMC111						
NMC811						

	Not Applicable					
	90-99% Yield & Grade					
	75-90% Yield & Grade					
	<75% Yield & Grade					

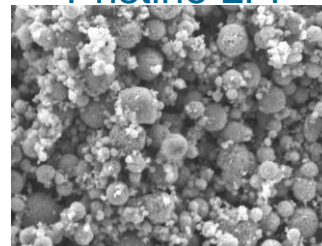
SEPARATION OF LFP AND NMC111 BY FROTH FLOTATION

- Separation of LFP/NMC111 (1:1 by weight) by froth flotation using Kerosene as collector
- The use of collector effectively increase the hydrophobicity of LFP particles, and consequently increase the separation efficiency to about 99%

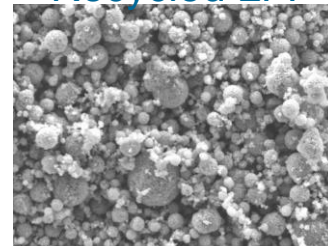
Product	Weight (g)	Composition (wt. %)	
		%LFP	%NMC111
Froth	9.25	99.18%	0.82%
Tailing	9.04	1.08%	98.92%



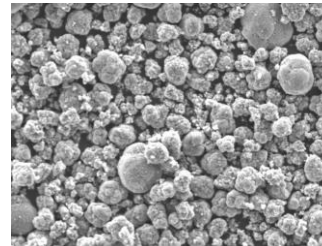
Pristine LFP



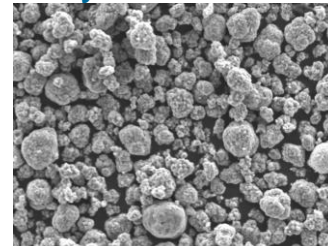
Recycled LFP



Pristine NMC111



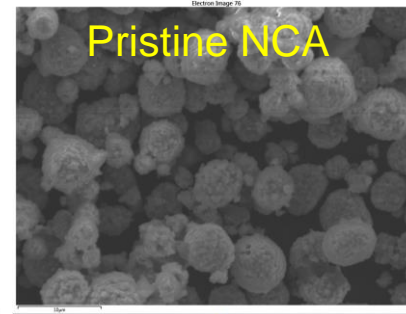
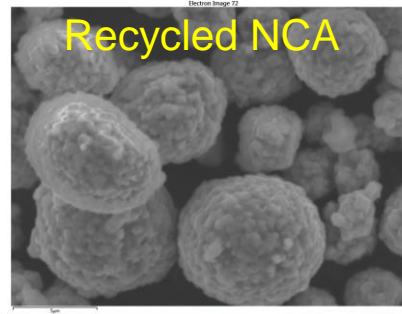
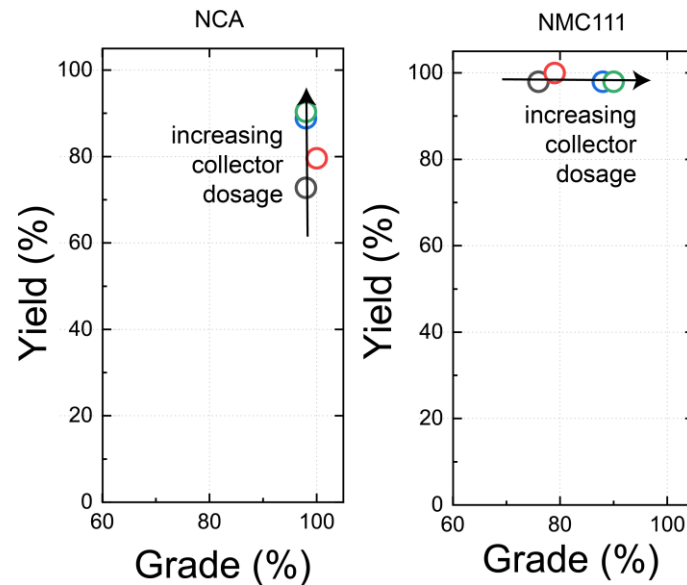
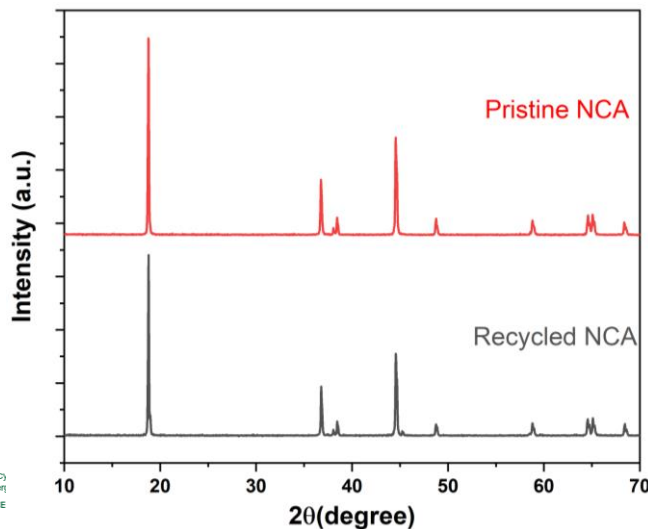
Recycled NMC111



SEPARATION OF NCA AND NMC111 BY FROTH FLOTATION

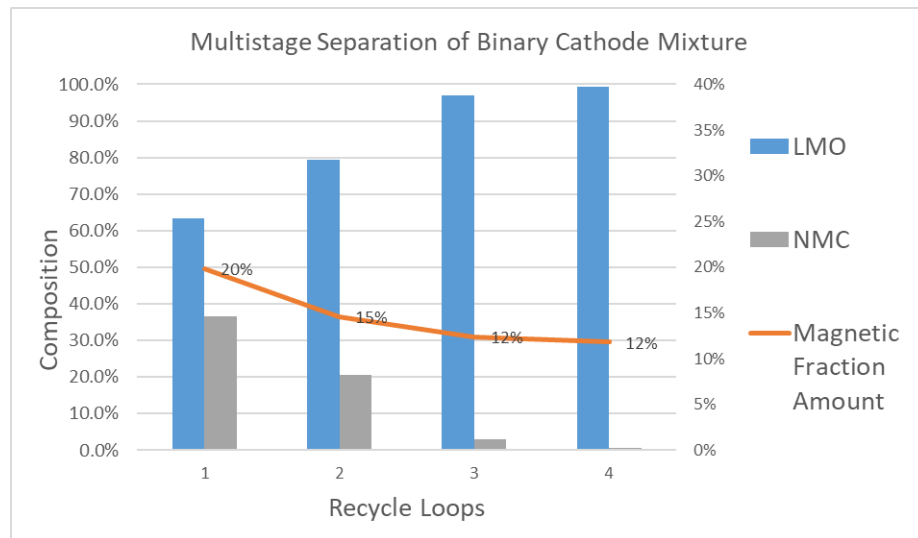
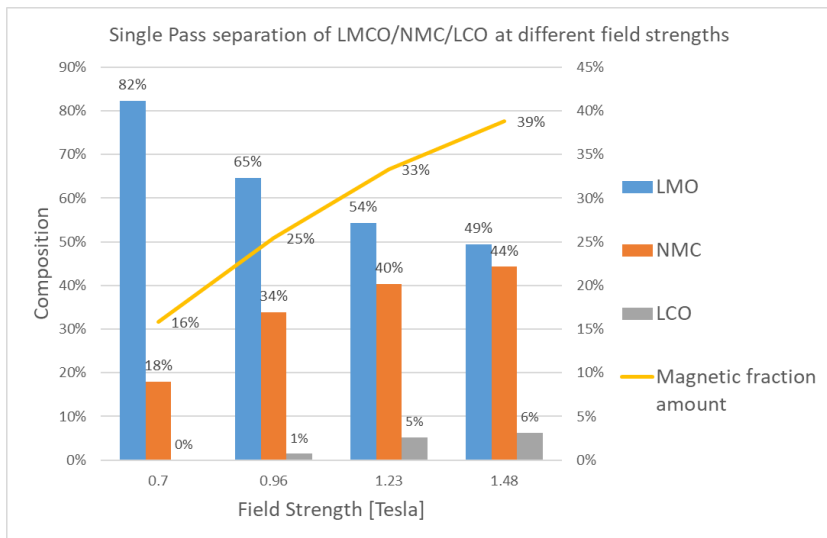
- Froth flotation process produces 98% purity of NCA materials from a binary NCA/NMC111 mixture with a recovery of 90.4%
- The recycling process maintains the original structure and morphology of cathode materials

Structure and morphology of recycled and pristine cathode materials



CATHODE SEPARATION – WET MAGNETIC

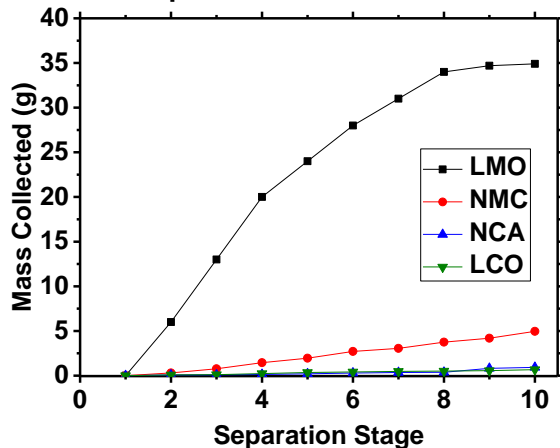
- Bench scale separation of mixtures of virgin cathode powders based on differing magnetic characteristics of components.
 - Separation of ternary mixture of LMO/NMC111/LCO
 - Selectivity of separation is highly dependent on magnetic field strength
 - Higher selectivity results in lower amounts of material collected in the magnetic fraction
 - High purity requires multiple passes through the separator



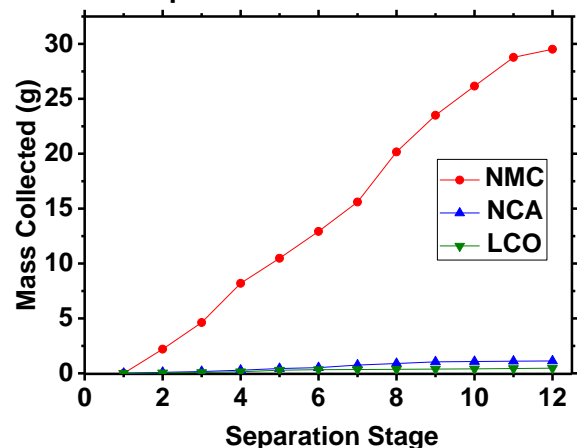
CATHODE SEPARATION – WET MAGNETIC

- Complete separation of multicomponent mixtures
 - Single components extracted at different field strengths
 - LMO at 0.8 T
 - NMC at 1 T
 - NCA at 1.4 T
 - Magnetic fraction recycled to high purity

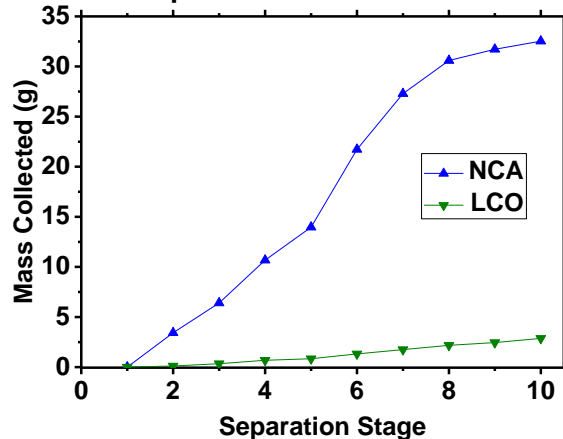
Step 1: Extraction of LMO



Step 2: Extraction of NMC



Step 3: Extraction of NMC

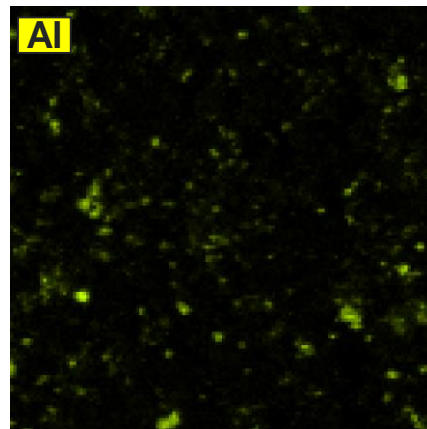
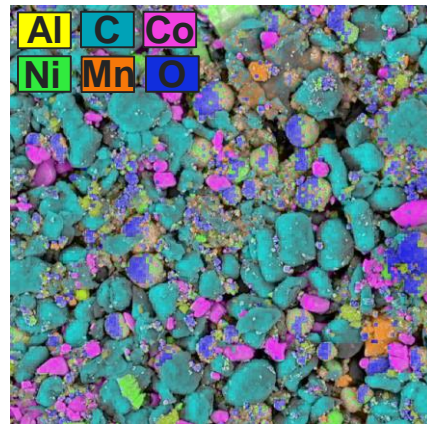


Final Result

Component	Final purity
LMO	97.4%
NMC	94.7%
NCA	91.9%
LCO	98.7%

UNDERSTANDING EFFECTS OF CONTAMINANTS

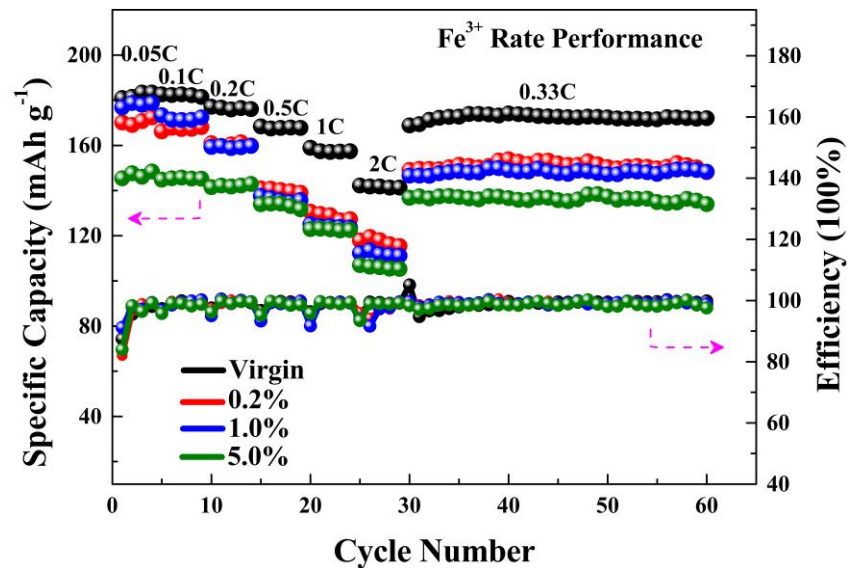
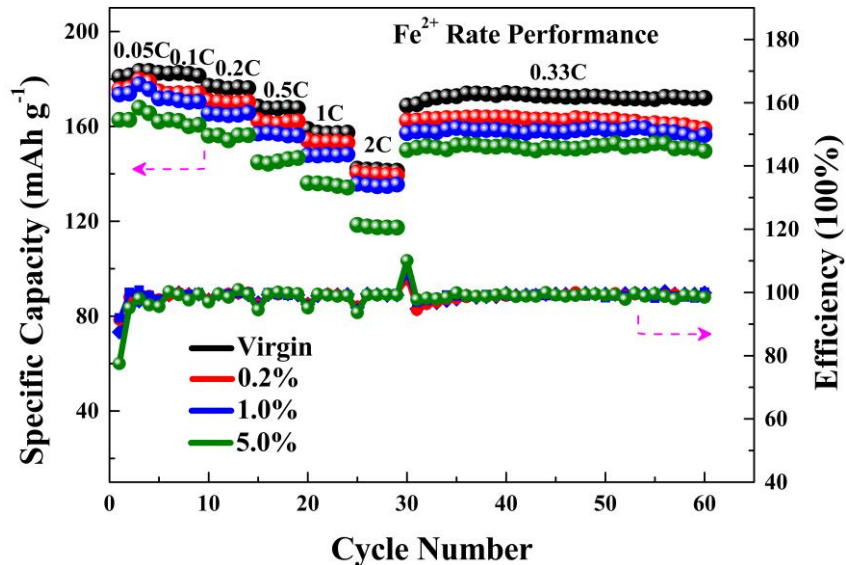
- Recovered materials are a complex mixture of materials
- Real materials will have contamination from various materials from the battery components
 - Al (cathode current collector)
 - Cu (anode current collector and connectors)
 - Fe (battery casing)
 - Other cathode materials
- Understanding the impact of these contaminants on the cathode material will enable contamination limits to be established
- Previously tested Al and Cu contaminates effects



EDX Maps of
Recovered Materials

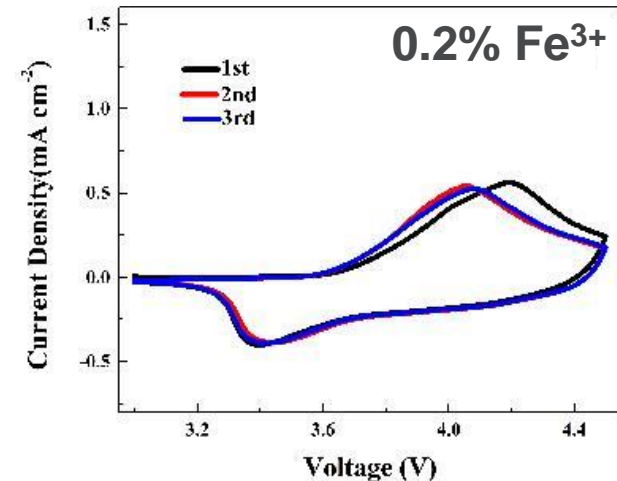
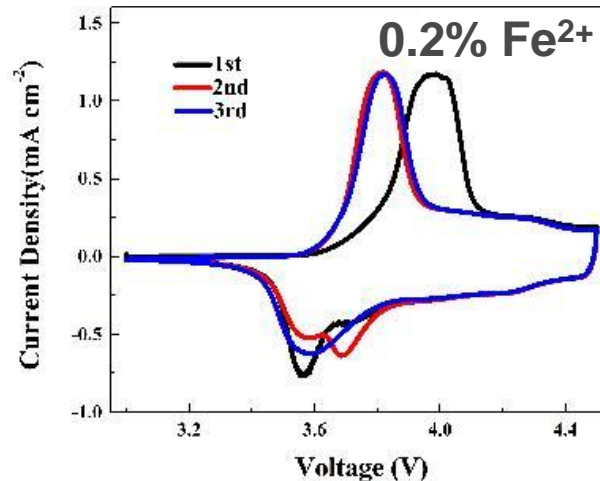
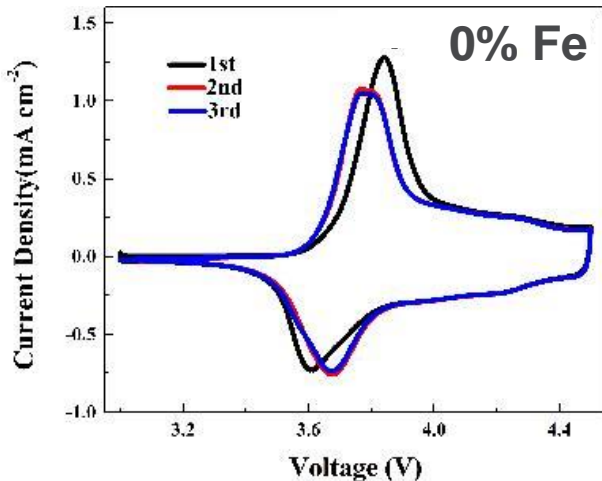
NMC622 CONTAMINATION STUDY – EFFECTS OF Fe AND OXIDATION STATE ON CYCLING

- Effects are strongly dependent on the Fe oxidation state
 - Fe^{2+} shows a small decrease in capacity that gets worse with high Fe content
 - Fe^{3+} causes a large reduction in rate performance



NMC622 CONTAMINATION STUDY – EFFECTS OF Fe AND OXIDATION STATE ON CV

- Effects are strongly dependent on the Fe oxidation state
 - Fe^{2+} shows small increase in peak separation and larger changes between 1st and 2nd cycles
 - Fe^{3+} causes a large reduction in current with a large increase in peak separation indicating high impedance to lithiation



PREPROCESSING FOR DIRECT RECYCLING – ACCOMPLISHMENTS AND RESULTS

- Created a one-step thermal process to effectively remove binder and relithiate cathode materials
- Developed separation techniques that can separate cathode materials to high purity
 - Froth flotation using various collector materials
 - Wet magnetic separation varying the magnetic field intensity and multiple passes
- Tested the effects of impurities on the performance of NMC 622 materials including the effects of impurity oxidation state
- For more information please see www.recellcenter.org, where our Quarterly Reports are posted.

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RECELL RECYCLING TOWN HALL

FRIDAY, JUNE 5, 2020 FROM 1:00 TO 3:00 (CENTRAL)

To continue the discussion the ReCell team will hold an interactive town hall meeting. Please join us at the BlueJeans session shown below and ask questions through Slido



Take a picture of
this slide

For Information
about ReCell



BlueJeans Meeting Access information

Computer

<https://bluejeans.com/749203749/9534?src=htmlEmail>

Phone

(866) 226-4650

Meeting ID: 749 203 749

Slido Q/A website

Computer or Smart Phone

www.Slido.com

Event Code

“recell”